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Microstructures of conducting polymers: Patterning and actuation study

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Abstract

The conducting polymers exhibit electrochemically driven expansion and shrinkage due to ingress and egress of dopant ions in response to potential applied. In this paper, we report on patterning of microdots and microsquares of polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,3-dihexyl-3-4-dihydro-2H-thieno[3,4b][1,4]-dioxepine PProDOT(Hx) 2 and their behaviour under voltage change. Stainless steel mesh was used to deposit microdots and inkjet-printed cellulose grids were used to deposit microsquares of the conducting polymers on the ITO surface. It was found that PPy showed distinct actuation in the z direction while colour change was prominent in the case of PEDOT and PProDOT(Hx)2.

Keywords

actuation, patterning, polymers, conducting, microstructures, study

Disciplines

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Microstructure of conducting polymers: patterning and actuation study

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Abstract

The conducting polymers exhibit electrochemically driven expansion and shrinkage due to ingress and egress of dopant ions in response to potential applied. In this paper, we report on patterning of microdots and microsquares of polypyrrole (PPy), poly (3,4-ethylenedioxythiophene) (PEDOT) and poly (3,3-dihexyl-3-4-dihydro-2H-thieno[3,4b][1,4]-dioxepine PProDOT(Hx)₂ and their behaviour under voltage change. Stainless steel mesh was used to deposit microdots and inkjet-printed cellulose grids were used to deposit microsquares of the conducting polymers on the ITO surface. It was found that PPy showed distinct actuation in the z direction while colour change was prominent in the case of PEDOT and PProDOT(Hx)₂.

Keywords: ITO glass, Ink-jet Printer, polypyrrole, poly (3,4-ethylenedioxythiophene), poly (3,3-dihexyl-3-4-dihydro-2H-thieno[3,4b][1,4]-dioxepine

1. Introduction

The conducting polymers exhibit electrochemically driven expansion and shrinkage due to ingress and egress of dopant ions in response to potential applied. The contraction and expansion of the conducting polymer can be converted to the rocking chair bending motion if a second layer, which does not change volume upon exposure to the electrochemical stimuli, is placed along with the conducting layer. During the electrochemical oxidation/reduction process the inert and flexible layer generates a stress gradient at interface due to the expansion/contraction of the conducting polymer film. This stress gradient causes a bending movement away from or toward the side of the conducting polymer film depending on voltage applied. This property has given conducting polymers a potential candidate to be used as a bioactuator. Most of the actuators have been constructed based on either bilayer [1] or trilayer configuration [2, 3] to achieve a bending movement. Adhesive tapes [4], polymer films [2, 3] and thin deposited metal layers [1] have been the materials most widely used as added films in bilayer and trilayer actuators. The trilayer actuators are capable of working in both air and liquid while bilayers are capable of working in liquid medium only.

Various useful properties, like conductivity, reversible oxidation, biocompatibility, hydrophobicity etc of conducting polymers make them desired materials for tissue engineering applications [5] also. The conducting polymers coating not only provide mechanical buffer between

the hard device and soft tissues and facilitate charge transport with various cationic and anionic species as done by nerve tissues but also they can be complexed with biologically active counter-ions and inflammatory drugs and lower the impedance of electrode in the bionic devices. Conducting polymers in the form of nanotubes structure has also been investigated for the controlled drug release application [6]. Several researches have been conducted to give certain morphology to the conducting polymer coatings. Yang et al. had investigated in giving porous morphology to the PEDOT films [7, 8] to improve biocompatibility of the material.

Because of the great energy separation (more than 3 eV) between the valence band and the conduction band, it is necessary to dope the conducting polymers to bring it to the conductive state. This doping process can be carried out in a reversible manner either chemically or electrochemically. Researchers have used two routes viz. chemical [9-15] and electrochemical [1-3] synthesis routes for the preparation of organic polymer actuators. While most of the PPy actuators have been synthesized by electrochemical routes [1-3], most of the PEDOT actuators have been synthesized by chemical routes [9-15].

Poorly defined chemical structure in which there is a significant amount of α - β' coupling limits the electrochemical response of PPy, hence, most of the researcher are interested in using commercially available (PEDOT). This polymer has a dioxyethylene bridging groups across the 3 and 4 position which blocks the possibility of α - β' coupling and consequently has much electrochemical stability [16]. While most of the researchers have focused on synthesis and characterization of the actuators based on PEDOT and PPy, none has considered comparing the performance of the actuator synthesized from these conducting polymers. Similarly, several researchers have focused on electrochromic [17], photovoltaic [18] and supercapacitors [19] applications of the PProDOT, none of works have been dedicated towards synthesizing and characterization of actuation behaviour of this polymer.

Conducting polymers are believed to have great impact in the field of electronic due to their mechanical flexibility and their potential for extremely low-cost device fabrication. Unlike organic semiconductor devices, conducting polymer devices do not have the expansive requirement of extreme environmental control. Also some of the soluble conducting polymers have potential to be used in inkjet printing for low-cost circuit fabrication, which is very attractive for the electronic industry.

Several types of techniques have been used till date to fabricate miniaturized conducting polymers and to obtain three dimensional nanoscale conducting polymers [20]. However, none of the works has been focused on understanding fate of the miniaturized conducting polymers

structure when voltage is applied to them. In this article, we report on patterning of microdots and microsquares of PPy, PEDOT and PProDOT(Hx)₂ and their actuation behaviour under voltage change. Stainless steel mesh was used to deposit microdots and inkjet-printed cellulose grids were used to deposit square and rectangle microstructures of the conducting polymers on the ITO surface. It was found that PPy showed distinct actuation in the z direction while colour change was prominent in the case of PEDOT and PProDOT.

2. Experimental

2.1. Chemicals and Materials

Pyrrole (Merck) was distilled and stored under nitrogen at -20 °C. 3,4-ethylenedioxythiophene was purchased from H.C. Starck. PEDOT-PSS (Orgacon dry) was purchased from Agfa.

2.2. Synthesis of ProDOT(Hx)₂ monomer

Synthesis of [ProDOT(Hx)₂] was carried out, following the literature [21] method with some modification. First 2,2-Dihexyl-propane-1,3-diol was synthesized by an alkylation of diethyl malonate using sodium hydride and the corresponding alkyl bromide followed by LiAlH₄ reduction.

Transesterification of 3,4-Dimethoxy thiophene with above diol resulted the corresponding 3,3-Dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxypine [ProDOT(Hx)₂] after twice purification by column chromatography. Bromination of [ProDOT(Hx)₂] resulted 6,8-Dibromo-3,3-Dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]-dioxypine[ProDOT(Hx)₂Br₂] and purified by column chromatography.

2.3. Ink-Jet printing

Ethylene cellulose grids were patterned over the ITO glass using ink-jet printer (Fujifilm Dimatrix Materials Printer (DMP-2800 Series)). The ink for the printer was prepared by dissolving ethylene cellulose in butanol and filtering the solution through 0.45µm micron syringe filter. The collagen micro-grids were printed by filling collagen solution into a custom designed 10pL cartridge equipped with a 16 nozzles print head. The whole cartridge was put into the printer and controlled by Dimatrix software to transfer pre-designed micro-grids onto the ITO glass. The solution was typically printed using a jet voltage of 25.0 V, a frequency of 5.0 kHz, and a customized wave-form.

2.4. Electrochemical synthesis of PPy, PEDOT and PProDOT(Hx)₂

The microdots and microsquares of the conducting polymers were synthesized using galvanostatic polymerization method. The masked ITO glass was used as working electrode and

stainless steel mesh was used as counter electrodes. A potentiostat/galvanostat (EG&G Princeton Applied Research Model 363) was used to generate constant current into polymerization solution. Monomer concentration and current density were 0.1M and 0.1mAcm^{-2} and the polymerization solutions were degassed before polymerization. 0.1M LiTFSI/PC (with 1% water) was used as an electrolyte solution and three different types of conducting polymers, PPY, PEDOT and PProDOTS were chosen for comparative study. PPY was polymerized at -32°C but PEDOT and ProDOTS were polymerized at room temperature as lower temperature poor quality deposits.

2.5. Electromechanical response of the actuators

Electromechanical response of the actuators under 0.1volts and 0.2Hz frequencies were observed in two different types of electrolyte solutions, 0.1M LiTFSI/PC and EMITFSI. Platinum mesh was used as counter electrode and Ag/Ag^{+} was used as reference electrode.

Datalogger (e-corder, ED821) was an interface unit between the computer and the potentiostat, which recorded a voltage signal applied to the bilayer actuator and associated current drawn. The actuator input voltage signals were provided by an eDAQ potentiostat 466 operating in a three-electrode mode. The displacement of the microdots and microsquares of the conducting polymers were observed using Leica inverted microscope.

3. Results and Discussion

In our preliminary study of bilayer actuators (**Figure 1**), we had compared displacement of the bilayer actuators comprising of chemically synthesized PEDOT-PSS and PProDOT(Hx)₂ with that of electrochemically synthesized one. The chemically synthesized conducting polymers were deposited on a gold coated PVDF membrane using spray coating technique. Similarly, electrochemically synthesized conducting polymers were deposited on a gold coated PVDF membrane using galvanostatic polymerization method. Thickness of the conducting polymer in both cases was same.

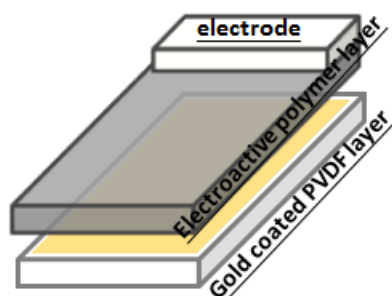


Figure 1. Schematic diagram of bilayer actuator.

It was found that displacement of electrochemically synthesized actuators showed far better displacement than the chemically synthesized ones (**Figure 2**). Electropolymerization technique has found to give the conducting polymer films that are highly conductive than the ones, which are polymerized by chemical polymerization technique. And as discussed earlier shrinkage and expansion of the conducting polymer is a function of amount of ions ingress and egress from it. The more ions enter in or out of the conducting polymer more shrinkage or expansion of the conducting polymer occurs, which result in greater displacement of the conducting polymers. Since electrochemically synthesized conducting polymers are more conducting, comparably more ions enter in or out of the polymer, resulting in more displacement. This is the reason for the better performance of the electrochemically synthesized actuators. So for the current study we chose electrochemically synthesized actuators to pattern and observe the actuation behaviour.

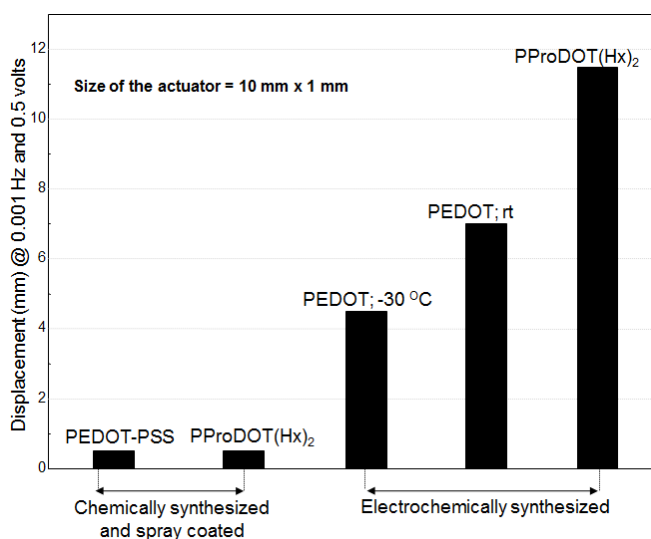


Figure 2. Displacement of bilayer actuators consisting of chemically and electrochemically synthesized conducting polymers.

Deposition of cellulose patterns on ITO glass

In order to pattern microsquare and microrectangular structures of conducting polymers on the ITO glass, ethylene cellulose patterns were used. The 5 layers of ethylene cellulose patterns were first deposited on the ITO glass from 0.5% solution of ethylene cellulose in butane. The ITO

glass was then heated at 50 °C for 1h to remove solvent and improve the adhesion of the layer on the ITO glass. **Figure 3** is the microscopic picture of the cellulose mask over the ITO glass used for the conducting polymer patterning.

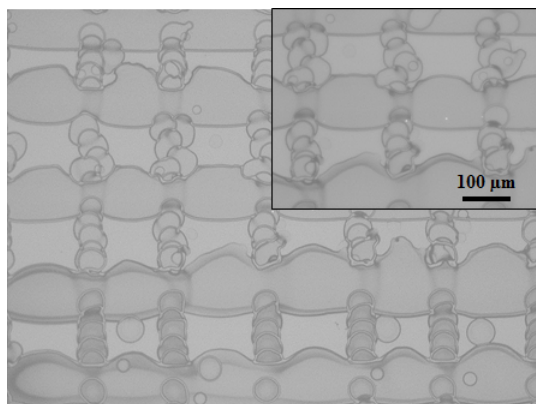


Figure 3. Ink-jet printed cellulose grids. Inset showing high magnification image.

Conducting polymer microstructures deposition on the ITO glass

Microsquares with different morphology (dots, squares and rectangles) of PPY, PEDOT and PProDOT(Hx)₂ were deposited on the ITO glass (**Figure 4 and 5**). In order to get dot morphology stainless steel mesh was closely attached to the ITO glass while in order to get square and rectangle structures of the conducting polymers, the cellular coated ITO glass was used. Cellulose was removed after polymerization by rinsing with acetone. The dots of PPY and PEDOT were around 60 micros while that of PProDOT were less than 30 microns. Similarly, squares and rectangle with length and width less than 150 microns were obtained.

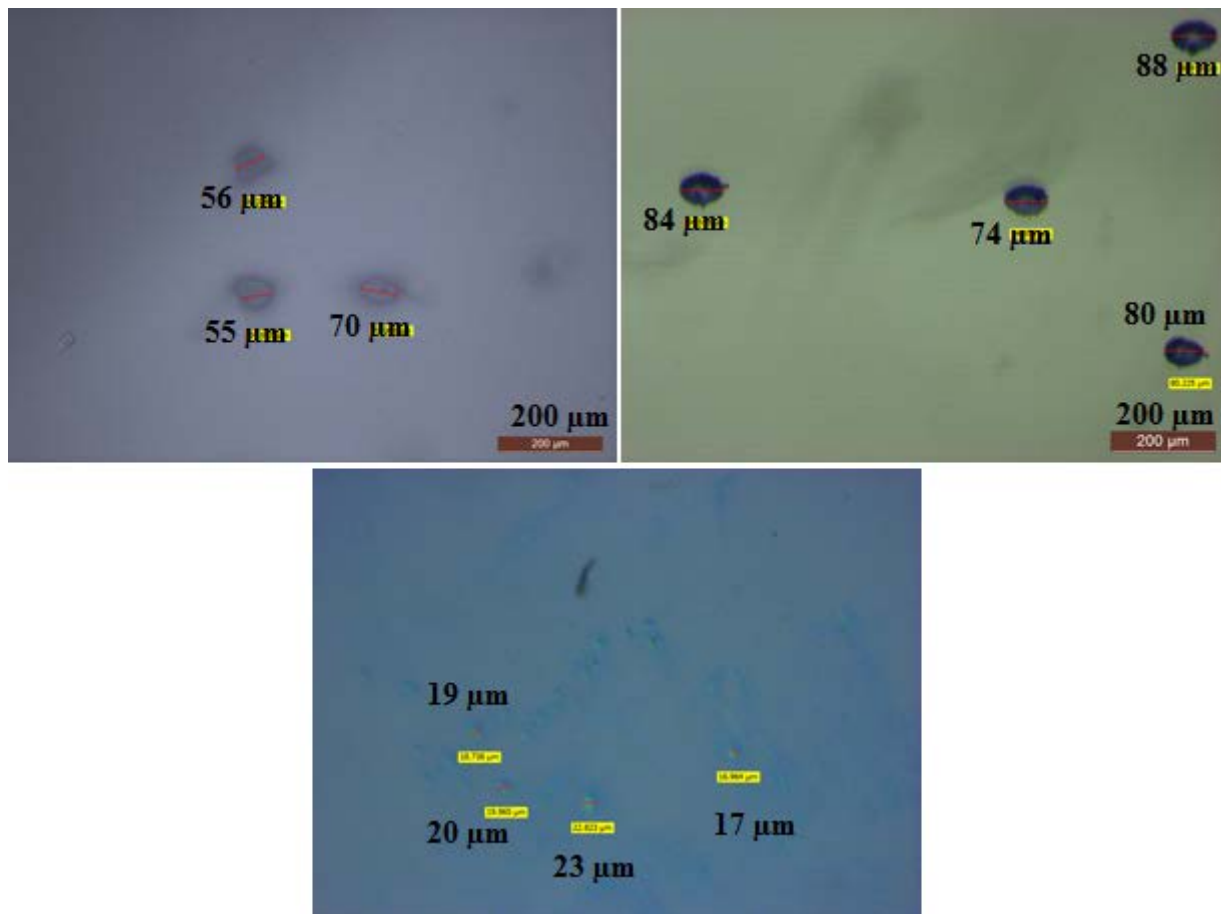


Figure 4. Microdots of PPY (top left), PEDOT (top right) and PProDOT(Hx)₂ (bottom) on ITO glass.

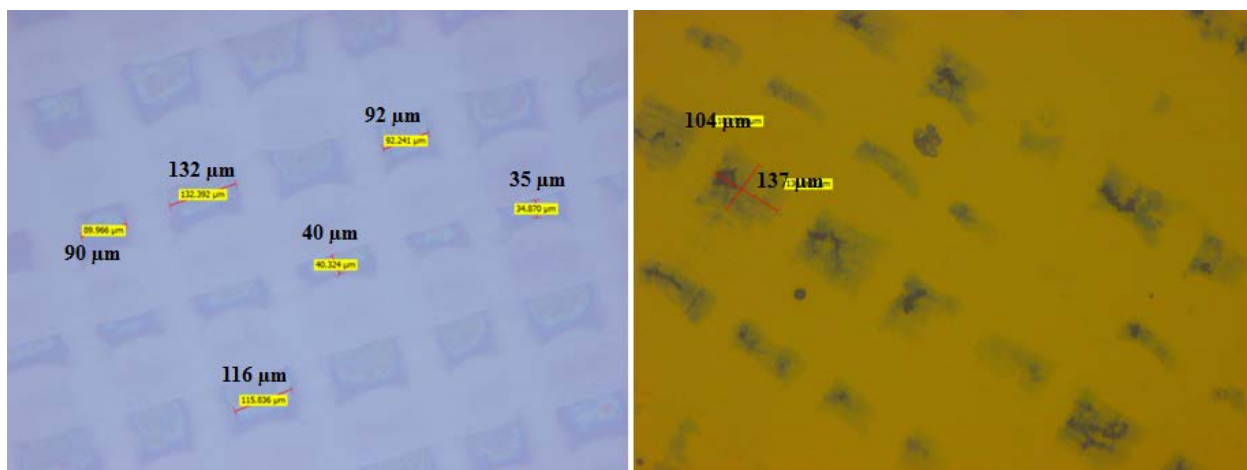


Figure 5. PPy (left) and PProDOT (right) microsquare and rectangle patterns on ITO glass.

Actuation of conducting polymer patterns

Actuation of these microdots and microsquares were done in a three electrode system and observed under microscope. **Figure 6** represents the schematic diagram of the system used. The

stainless steel mesh was used as a counter electrode and Ag/Ag⁺ was used as a reference electrode. Conducting polymer coated ITO glass was placed facing down ward and inverted microscope was used to observe morphology change. (peter can you explain more about this setup?)

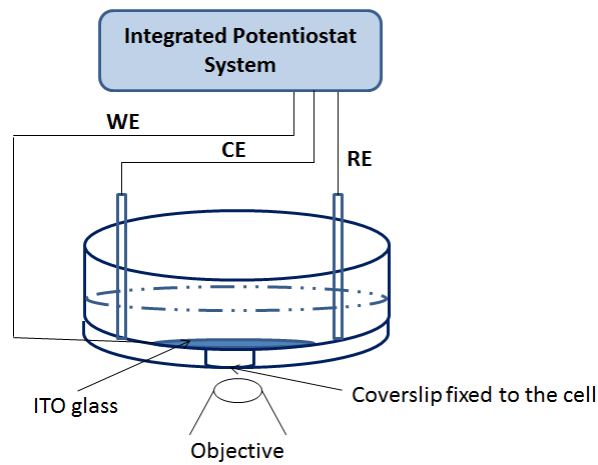


Figure 6. The three electrode cell used for the actuation study.

Figure 7 represents the actuation of the microdots at ± 1 volts. The actuation experiment revealed that the actuator was displacing in vertical direction as shown. The vertical displacement was clear in the case of PPY while colour change was more prominent in PEDOT.

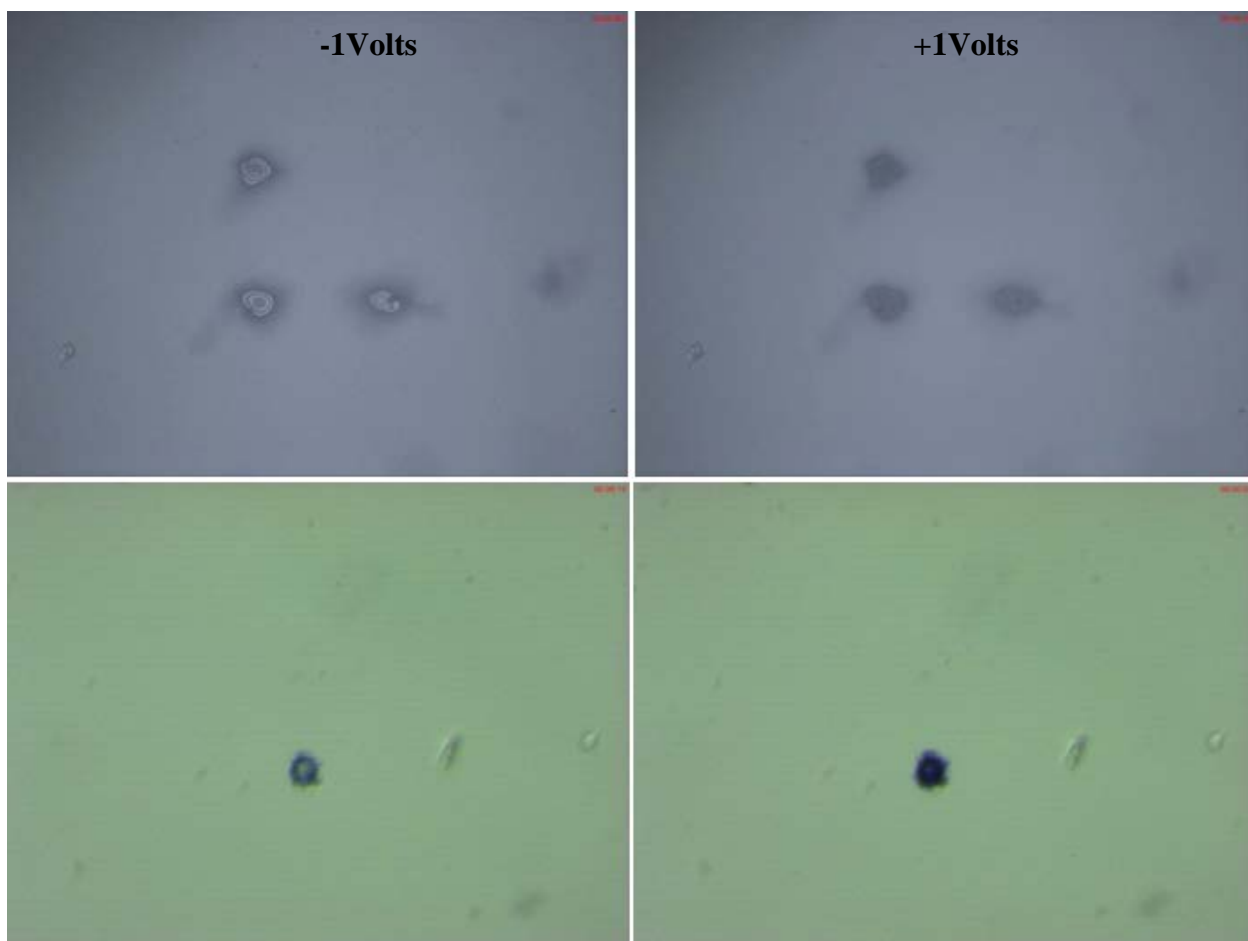


Figure 7. Electrochemical response of the microdots of PPy(Top) and PEDOT (bottom) at ± 1 volts.

Figure 8 represents the electrochemical response of the micro squares and rectangles to the voltage applied. As in the case of microdots, the PPy showed clear vertical actuation. Furthermore, some side of the microsquares and rectangles peeled of the substrate and showed back and forth motion on alteration of voltage. On the other hand, colour change rather than actuation was more prominent in the case of PProDOT.

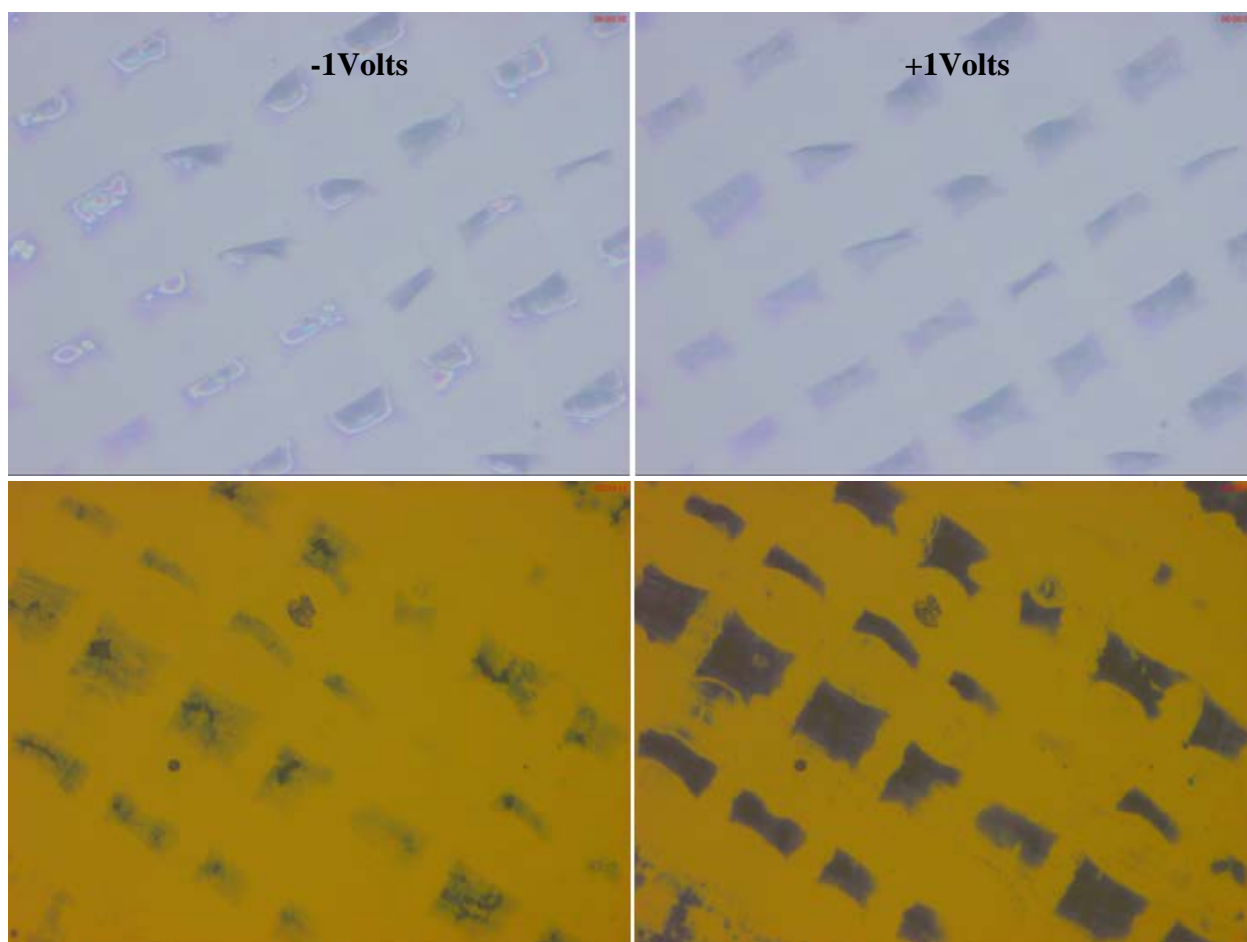


Figure 8. Electrochemical response of the microsquares and microrectangles of PPy(Top) and PEDOT (bottom) at ± 1 volts.

4. Conclusion

Micro structures of electrochemically synthesized PPy, PEDOT and PProDOT(Hx)₂ were deposited on the ITO glass and effect of voltage change on the morphology of the microstructures were observed. It was found that PPy showed clear shrinkage and expansion while voltage was alter from +1 volts to -1 volts. In the other hand, colour change was more prominent in the case of PEDOT and PProDOT(Hx)₂

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